

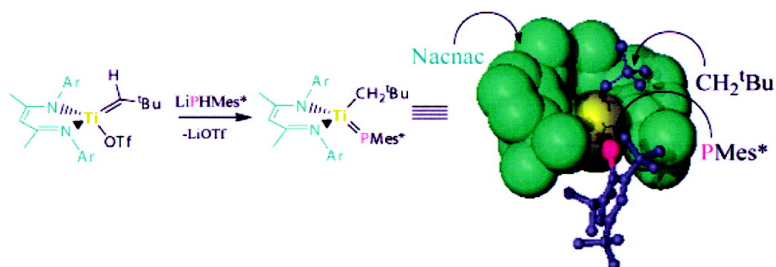
Communication

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Four-Coordinate Phosphinidene Complexes of Titanium Prepared by α -H-Migration: Phospha-Staudinger and Phosphaalkene-Insertion Reactions

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Chemistry of transition-metal complexes containing the terminal phosphinidene¹ functionality is exceedingly underdeveloped when compared to the lighter nitrogen congener.² In contrast to imide-group transfer reactions, the concept of phosphinidene-group transfer has received far less attention, presumably due to the lack of stable systems having this functionality. Examples of early-transition metal phosphinidenes include only a handful of complexes composed of Zr^{3–5} and Ta.^{6,7} Other isolable phosphinidenes of the early-metal series include some in group 6 (e.g., Mo and W).^{8–10} Akin to early-transition metals, the mid- to late-transition metal phosphinidenes are also infrequent, yet of great interest, because these systems can demonstrate a direct contrast between electron-deficient and -rich complexes possessing this common functionality. Rare examples of the latter family of elements include Fe,¹¹ Ru,^{12,13} Os,¹³ Co,¹⁴ Rh,¹⁴ Ir,^{14,15} and Ni.¹⁶ In most of these compounds, encumbering substituents on P are required, unless otherwise stabilized electronically with electron-rich groups.^{1,17} Hitherto, the only isolable group 4 terminal phosphinidenes reported to date are the bis-cyclopentadienyl derivatives described by Stephan³ and Protasiewicz.⁴

Our recent report of the synthesis of four-coordinate titanium alkylidene¹⁸ and imido^{18,19} complexes stimulated the pursuit of an analogous titanium phosphinidene. Titanium phosphinidenes are unknown,^{3d} presumably due to hard–soft mismatch of these elements. Herein, we report the first titanium complex containing a terminal phosphinidene ligand. Judicious choice of substituent on P can influence the kinetic stability of the reactive [Ti=PR] fragment.

A strategy for preparing a low-coordinate and terminal titanium phosphinidene complex involved treatment of the nucleophilic and four-coordinate titanium alkylidene (Nacnac)Ti=CH^tBu(OTf)¹⁸ (Nacnac[–] = [Ar]NC(Me)CHC(Me)N[Ar], Ar = 2,6-*i*-Pr₂C₆H₃) with the corresponding primary lithium phosphide. When 1 equiv of LiPHR (R[–] = Cy, Trip; Cy = C₆H₁₁, Trip = 2,4,6-*i*-Pr₃C₆H₂) is added to a cold ether solution of (Nacnac)Ti=CH^tBu(OTf), the color rapidly changes from red-brown to orange-brown. After workup, complex ([Ar]NC(Me)CHC(Me)P[R][CH₂^tBu])Ti=NAr(OEt₂) (**1**) (R[–] = Cy, **1a**, 76% yield; R = Trip, **1b**, 89% yield) is isolated as a dark-brown powder (Scheme 1).²⁰ As an example, the ¹H NMR spectrum of **1b** is consistent with these species having C₁ symmetry, while the ³¹P NMR shows only one diastereomer present (–43 ppm).²⁰

Large dark-orange blocks of **1** were grown from a saturated pentane solution, and their connectivity was determined from single-crystal X-ray diffraction methods.²⁰ Both complexes are isostructural and reveal a five-coordinate titanium complex in a highly congested and distorted square pyramidal environment where the labile OEt₂ ligand occupies an axial site.²⁰ Upon inspection of the structure of **1b** (Figure 1), it is evident that the [PTrip] fragment has undergone migration to the β -carbon of the former Nacnac[–] ligand. The short Ti1–N41 distance (1.732(6) Å) is clearly indicative of a Ti–N_{imide}

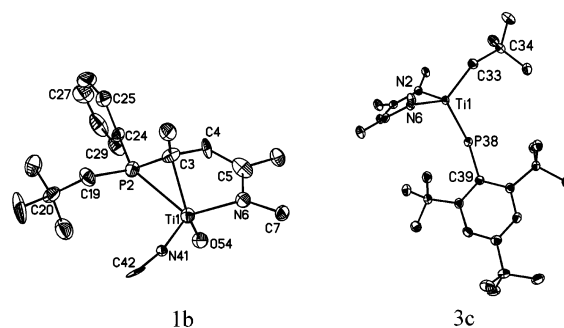
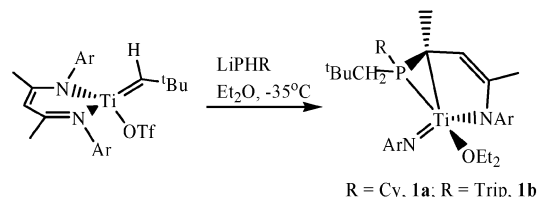


Figure 1. Molecular structures of **1b** and **3c** with thermal ellipsoids at the 50% probability level. Ethyl groups on O54 and ^tPr groups on the P-Trip in **1b** (C25, C27, C29) have been omitted. Aryl groups in **1b** and **3c** with the exception of the *ipso*-carbons on the nitrogens have been also omitted for clarity.

Scheme 1. Synthesis of **1a** and **1b**

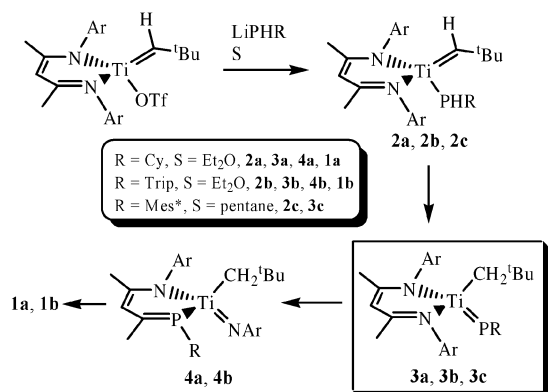


multiple bond.² Both P2 and C3 are bound to Ti1 (2.572(3) and 2.123(8) Å, respectively), while the prior neopentylidene α -carbon C19 has acquired an additional proton and is now attached to the phosphorus as an alkyl group.²⁰ Because of the low-coordination environment on Ti, close interactions between the titanium center and the olefinic carbons of the chelate ligand are also noted in the structure of **1b** (Ti1–C4, 2.420(8) Å; Ti1–C5, 2.456(9) Å).

Formation of **1** is proposed to occur via transmetalation of LiPHR with (Nacnac)Ti=CH^tBu(OTf) to furnish putative neopentylidene-phosphide (Nacnac)Ti=CH^tBu(PHR) (**2**) (R = Cy (**2a**); R = Trip (**2b**)), which subsequently undergoes α -H-migration to give phosphinidene (Nacnac)Ti=PR(CH₂^tBu) (**3**) (R = Cy (**3a**); R = Trip (**3b**)) (Scheme 2). Considered quite reactive, intermediate **3** rearranges through a “phospha-Staudinger” reaction to generate the titanium-imide complex supported by the NP hybrid ligand ([Ar]NC(Me)CHC(Me)P[R])Ti=NAr(CH₂^tBu) (**4**) (R = Cy (**4a**); R = Trip (**4b**)). Precedent for “Wittig or Staudinger-type” reactions at the imine functionality of the Nacnac[–] ligand has been reported previously by our group.¹⁸ Consequently, complex **1** would then form from **4** by phosphaalkene insertion into the Ti–CH₂^tBu bond (Scheme 2). The latter reaction would be consistent with traditional phosphaalkene chemistry because there is positive charge at the P atom resulting from polarization in the σ bond.^{1d}

Evidence for the intermediates generated during the formation of **1b** is substantiated by monitoring the reaction mixture at low temperature using ³¹P NMR spectroscopy.²⁰ Upon thawing of the

Scheme 2. Proposed Intermediates along the Reaction Pathway To Generate **1a** and **1b**



reagents in Et₂O to $-20\text{ }^{\circ}\text{C}$, a resonance assigned to **2b** (19 ppm, $J_{\text{P-H}} = 556\text{ Hz}$, purple solution)²¹ is observed. From -18 to $-5\text{ }^{\circ}\text{C}$, the solution changes to green, and two resonances centered at 337 and 285 ppm are generated which vanish quickly to form a resonance at 153 ppm. All three resonances lack P–H coupling, thus consistent with formation of **3b** and **4b**, respectively. The two downfield shift peaks for **3b** are suggestive of two isomers being present in solution (vide infra). Warming above $-5\text{ }^{\circ}\text{C}$ causes a color change to red-brown and generates the resonance corresponding to **1b** (vide supra), concurrent with disappearance of the downfield shifts attributed to **3b** and **4b**.²⁰

In an effort to kinetically stabilize titanium-phosphinidene **3**, a likely intermediate generated from the reaction to form **1**, (Nacnac)Ti=CH^tBu(OTf) was treated with the bulkier phosphide LiPHMes* (Mes*⁻ = 2,4,6-^tBu₃C₆H₂) in pentane at $-35\text{ }^{\circ}\text{C}$ (Scheme 2). Accordingly, complex (Nacnac)Ti=PMes*(CH₂^tBu) (**3c**)²⁰ is isolated in good yield ($\geq 78\%$), inasmuch as intermediate (Nacnac)Ti=CH^tBu(PHMes*) **2c** is observed to form and decay when monitoring the reaction mixture (³¹P NMR: Et₂O, $-10\text{ }^{\circ}\text{C}$, 31 ppm, $J_{\text{P-H}} = 555\text{ Hz}$).^{20,21} Unlike putative **3a** and **3b**, phosphinidene **3c** is relatively stable both in solution and in the solid state, therefore suggesting that **3c** is the kinetic product while **1a** and **1b** are thermodynamic products. Large blocks of dark-green **3c** were grown from pentane, and the molecular structure is depicted in Figure 1.²⁰ The structure of **3c** displays a four-coordinate titanium-phosphinidene complex with a super short Ti=P bond (2.1831(4) Å)²² and a linear Ti=P–C_{ipso} angle (164.44(5)^o). Examples of linear M=P–R phosphinidene species are exceedingly rare and often arise from formation of a pseudo-triple bond.^{1,6,9} ³¹P NMR solution spectra of **3c** manifest two resonances at 242 and 216 ppm, also consistent with two isomers present in solution. Formation of these isomers could occur for steric reasons or by deviation of the “Ti=PAR” fragment from the NCCCN ligand plane.²³ Unfortunately variable-temperature ³¹P NMR (25 – $40\text{ }^{\circ}\text{C}$) leads to decomposition instead of interconversion between the two isomers.

In summary, we have shown that the four-coordinate titanium neopentylidene can engage in α -deprotonation of phosphides to yield reactive four-coordinate Ti(IV) phosphinidene species. The titanium-phosphinidene complexes presented in this work are close analogues of traditional phosphalkenes, differing simply by the presence of accessible d-orbitals.

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Supporting Information Available: Complete experimental preparation and crystallographic data for compounds **1**–**4** and the OEt₂-free adduct of **1b** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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